NATURAL SOLID BITUMENS AS POSSIBLE ANALOGS OF COMETARY AND ASTEROID ORGANICS

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Summary: The study of the cometary nucleus composition will be one of the main goals of „Rosetta" mission. To interpret the spectral properties of cometary surface one needs to have spectral library of the relevant materials, in particular, organics. For this purpose we have performed the spectral reflectance measurements of natural solid oil bitumens (asphaltites, kerites, anthraxolites). The samples were also characterized by chemical analyses, solid-state ^{13}C-NMR, and X-ray diffractometry. In the NIR region the spectral parameters have been found, which make it possible to spectrally derive carbon aromaticities (f_a), H/C or C/(C+H+N+S+O) atomic ratios, and even some structural properties.

Background: The observations of P/Halley have demonstrated that cometary nucleus is heterogeneous and consists of bright and dark materials. Brighter components could be interpreted as ices, while darker materials are represented by the assemblages composed of refractory organics and inorganics [e.g., 1]. The composition of organic components of primitive meteorites and IDPs [e.g., 2], infrared observations of comets and the mass-spectrometry of P/Halley CHON dust particles [e.g., 3] suggest that cometary refractory organics probably consist mainly of complex mixture of various hydrocarbon polymers. The natural solid oil bitumens have been shown to be useful as terrestrial analogs of meteoritic and asteroid organics [4,5,6,7]. The continuous sequence of solid bitumens includes wurtzilites, asphaltites (gilsonites, glance pitches, grahamites), kerites (albertites, impsonites) and anthraxolites (from low to high) [8]. These dark solids are complex mixtures of organic compounds, most of which are aliphatic and polycyclic aromatic hydrocarbons (PAHs). The sequence represents a wide range of compositions and structures - from largely amorphous aliphatic-rich wurtzilites and asphaltites to more structurally ordered and thermally processed high anthraxolites (shungites) composed mostly of condensed aromatic polymer. This diversity makes it possible to match extraterrestrial organics of various compositions with different extent of thermal evolution. We suggest that cometary refractory organics, being more primitive, more volatile-rich than asteroid organics, may be similar to asphaltites in many respects. When the short-period comet becomes "older", the surface of its nucleus should gradually lose volatiles, and in extreme case this thermally processed surface crust would compositionally resemble high anthraxolite or graphite.

Experimental: The specimens of a suit of natural bitumens were ground and sieved to size fraction <25 µm. In some cases more size fractions have been prepared to study the particle size effects. The biconical reflectance spectra of the powdered samples were recorded in the range of 0.5-16 µm using Bruker IFS88 FTIR-spectrometer. The measurements were performed relative to spectralon and rough gold standard in the H_2O and CO_2 purged atmosphere. The samples were chemically analyzed for C, H, O, N, and S. Solid state CP-MAS ^{13}C NMR was employed to derive carbon aromaticities (f_a). The samples were also characterized by X-ray diffraction (XRD) to estimate structural parameters and a fraction of ordered aromatic structures.

Results: In general, the data are consistent with those obtained previously for other samples of the same kind [4,5]. The IR reflectance spectra of the most H-rich specimens (asphaltites, low-kerites) show various fundamental absorptions due to aliphatic and aromatic C-H stretching and bending, as well as overtones and combinations of these fundamentals. The increasing aromaticity accompanied by decreasing H-content results in the drop in intensity of aliphatic absorption features relative to aromatic ones. The spectral slope in the VIS-NIR region gradually decreases with increasing aromaticity and carbonization, as expected [4,5]. The spectra of the most carbonized materials - high anthraxolites (shungites) - are flat and featureless both in visible and in the inrfared spectral regions. Although the spectral slopes and absorption band depths do show correlation with composition and structure, we found that it is not easy to derive quantitative compositional information (for example, f_a) using these spectral reflectance parameters. In particular, both slopes and band depths are particle size dependent. In addition, the absorption features due to vibrations of various aliphatic and aromatic functional groups are often overlapped with each other and with other absorptions due to O-bearing groups.

However, in the NIR region we found 2 spectral parameters, which show strong correlation with aromaticity and chemical composition, and even with some structural parameters. Moreover, the use of these parameters makes it possible to see if some mineral admixtures are present. The bitumen spectra display a complex absorption feature near 2.3-2.6 µm (Fig.1) due to combinations and overtones of various fundamental modes which occur in the mid-infrared. These absorptions are mostly due to aliphatic CH_2 and CH_3 groups, though the contribution of aromatic

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and O-bearing groups is also possible. We discovered that the wavelength position of local reflectance maximum at 2.2 μm ($max_{2.2}$) moves to longer wavelengths with increasing f_a. Shown in Fig. 2 is the correlation between the position of this reflectance maximum and aromaticities determined by NMR. The use of a linear least squares fit allows to spectrally derive f_a of pure bitumens with rather good accuracy (the average deviation from actual f_a determined by NMR is 2-3% and doesn't exceed 4%). For the samples with mineral impurities the results are less accurate with maximal error of 12% for the bitumen mixture containing about 40% of inorganics - mostly carbonates. The presence of mineral components usually results in the overestimation of f_a. Another useful spectral parameter is the ratio of reflectance values at the maxima around 2.3-2.6 μm absorption feature (Fig.1, 3). The R_2/R_1 ratio rises with increasing aromaticity, since the long wavelength absorption edge of the broad aromatic absorption feature centered in the UV region is known to shift to longer wavelength with increasing condensation of aromatic structures. The use of this parameter gives somewhat less accurate results, and this value is particle size dependent. The presence of mineral admixtures in all cases causes the underestimation of f_a. The difference between f_a values, determined using these 2 parameters doesn't exceed 0.06 (6%) for relatively pure organic samples, while for 4 samples with mineral impurities this difference is 0.12-0.19. So the combination of 2 parameters allows to see if some inorganics are present. The averages of f_a values estimated from both parameters show very small difference from f_{aNMR} even for "dirty" samples (0-0.04) except for one sample (0.11). Since aromaticities of oil bitumens correlate with chemical composition (H/C or C/(C+H+N+S+O) ratios) and structure, the same spectral parameters can be used to evaluate these properties. For example, Fig.4 shows a positive correlation between $max_{2.2}$ and C/(C+H+N+S+O) atomic ratios. Few "dirty" samples depart from linear square fit, since the admixtures of carbonates and silicates contribute to C and/or O contents. In addition, the $max_{2.2}$ correlate with some structural parameters determined by XRD. The $max_{2.2}$ shows a negative correlation with d_{002} and positive correlation with aromatic crystallite size L_c. Some positive correlation between the $max_{2.2}$ and the fraction of structurally ordered aromatic carbon also exists though the scatter of data points doesn't allow to derive this value from reflectance spectra with good accuracy. It should be noted, that the calibrations described here are applicable only for those materials which display absorption features near 2.3-2.6 μm (fa ≤ 0.6).

Conclusion: The spectral parameters provide an excellent opportunity to estimate aromaticities, chemical composition and even some structural properties of natural organic materials if they show absorption features near 2.3-2.6 μm. The studies of how the admixtures of various relevant minerals may affect these spectral parameters are in progress.

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Fig.1 — Scaled Reflectance vs Wavelength (microns), with $max_{2.2}$, R_1, R_2, fa=0.50, fa=0.33, fa=0.13

Fig.2 — Local max near 2.2 microns vs Aromaticity (fa); y = 2.17 + 0.13 x, r^2 = 0.95; "pure organics", "dirty" samples

Fig.3 — R2/R1 vs Aromaticity (fa); y = 0.744 + 0.945x, r^2 = 0.934; "pure organics", "dirty" samples

Fig.4 — Local max near 2.2 microns vs C/(C+H+N+S+O)(at.); y = 1.986 + 0.563x, r^2 = 0.988; "dirty" samples, "pure organics"